SIMS MEASUREMENT OF MAGNESIUM ISOTOPIC RATIOS IN ALH-77278 AND -77307 CHONDRITES

Hiroshi Nishimura and Jun Okano

*Institute of Geological Sciences, College of General Education,
Osaka University, 1-1, Machikaneyama-cho, Toyonaka 560*

Abstract: Isotopic ratios of $^{24}Mg/^{25}Mg$ and $^{26}Mg/^{25}Mg$ have been measured for Mg-rich and Al-poor portions of matrix areas of ALH-77278 and -77307 meteorites by ion microprobe mass spectrometry. The magnesium isotopic ratios for the meteorites were compared with that for a terrestrial forsterite of laboratory standard. Clear excesses of ^{24}Mg up to 10 permil have been found for the portions where concentration ratio of Al/Mg was less than 0.1 and that of Mg/Si was between 1.8 and 2.2.

1. Introduction

It has become considered that the primordial solar nebula was isotopically inhomogeneous and consisted of two or more components from the observations of excess ^{26}Mg due to the decay of now-extinct ^{26}Al in the Allende and Leoville carbonaceous meteorites by several investigators (Gray and Compston, 1974; Lee and Papanastassiou, 1974; Lee *et al.*, 1976, 1977a, b; Stegmann and Begemann, 1981). Furthermore, excess ^{24}Mg has been reported for Mg-rich and Al-poor portions of matrix in the Allende and Yamato-74191 chondrites (Nishimura and Okano, 1981a, b, 1982). These isotopic anomalies of magnesium as well as the excess ^{16}O led us to a hypothesis that such isotopes would have been synthesized during a supernova explosion which could have been estimated to explode $1-3 \times 10^6$ years prior to the crystallization of the minerals in which the excesses were found.

In order to search for further experimental evidence of excess ^{24}Mg in other primitive meteorites, magnesium isotopic ratios have been measured for the samples of ALH-77278 (LL3) and ALH-77307 (C3) meteorites. The results will be described in the following.

2. Experimental

A Hitachi IMA 2A ion microprobe mass analyzer was used for the isotope analysis. A 12 keV oxygen primary ion beam was used. The diameter and the current of the beam on the sample surface were 80 to 200 μm and 0.2 to 3 μA, respectively. The ultimate pressure in the sample chamber was about 5×10^{-6} Pa, and the pressure during the measurement was about 4×10^{-5} Pa.

Samples used in the present work were ALH-77278 (LL3), ALH-77307 (C3) and a terrestrial forsterite in dunite from Ehime Pref., Japan. This forsterite has been used

as a laboratory standard.   Polished and ultrasonically cleaned surfaces of these samples were used for the analysis.

Magnesium isotopic analyses were performed for the Al-poor portions where the concentration ratio of Al/Mg was less than 0.1, in order to avoid the complexity due to the possible mixing of the daughter of [26]Al, and to be able to look for the [24]Mg excess.   Mass scanning was repeated 30 to 50 times at one probed portion over the range of mass number 24 to 26.   Peaks of [23]Na, [27]Al and [28]Si were also recorded for each probed portion for the purpose of estimating the concentration ratios of Al/Mg and Mg/ Si.   In order to neutralize the charge build-up due to the positive ion bombardment, electron spray was applied, and the surface of the sample was covered with a sheet of tantalum with apertures of about 3 mm in diameter.   In order to decrease the contribution of interfering molecular ions originated from volatiles such as hydrocarbons and water vapor to the mass peaks at mass numbers 24, 25 and 26, a cold finger of liquid nitrogen was put aside the sample holder.   This cold finger remarkably decreased the contribution of interfering molecular ionic species.   In the case of [24]MgH$^+$, the order of the contribution was evaluated to be about 4×10^{-4} as [24]MgH$^+$/[25]Mg$^+$ (NISHIMURA and OKANO, 1982).

The fractions of interfering multiply-charged ions to the subject ionic species have been also extensively examined (NISHIMURA and OKANO, 1981a, b, 1982), and the contribution was found to be less than 1×10^{-3} as a whole.

The control of the detecting system, the calculation of data and the statistical procedures were done by a microcomputer system developed by the authors.   The description of hardwares and softwares of the computer system appeared elsewhere (NISHIMURA and OKANO, 1982).

The [24]Mg/[25]Mg and [26]Mg/[25]Mg ratios were calculated from the raw secondary ion intensities and the deviations of these ratios from those for the terrestrial forsterite sample (laboratory standard) were also calculated as delta values according to eq. (1).

$$\Delta_{m/25} = \left(\frac{(^m\mathrm{Mg}/^{25}\mathrm{Mg})_s}{(^m\mathrm{Mg}/^{25}\mathrm{Mg})_r} - 1 \right) \times 1000, \quad (m=24, \ 26) \tag{1}$$

where subscripts s and r represent sample and reference, respectively, and $(^{24}\mathrm{Mg}/^{25}\mathrm{Mg})_r$ $= 7.99345 \pm 0.00035 (\sigma_m)$ and $(^{26}\mathrm{Mg}/^{25}\mathrm{Mg})_r = 1.08784 \pm 0.00068 (\sigma_m)$ for the terrestrial forsterite of a laboratory standard.

The reproducibility of magnesium isotopic measurement was carefully checked by the examination of the data obtained for the laboratory standard for a long period of time.   The reproducibility was confirmed to be within 3 permil as twice as much the standard deviation for the measurement during two years.

3.   Results and Discussion

The results obtained for ALH-77278 and -77307 are shown in Table 1, Figs. 1 and 2.   In Table 1, isotopic ratios of [24]Mg/[25]Mg and [26]Mg/[25]Mg as raw peak height ratios and their standard deviations (σ_m) are shown in the first column, and Δ values calculated from eq. (1) are listed in the second column.   Atomic ratios of Al/Mg and Mg/Si are also shown in the table together with the raw secondary ion intensities of [27]Al$^+$/[24]Mg$^+$

Table 1. Magnesium isotopic ratios, delta values and ratios of Al/Mg and Mg/Si
obtained for ALH-77278 and -77307 chondrites.

	R24/25	R26/25	Δ24/25	Δ26/25	R27/24	Al/Mg	R24/28	Mg/Si
ALH-77278 (LL3)								
1	8.002(12)	1.0866(17)	1.1(1.5)	−1.2(1.5)	0.024	0.013	1.87	1.21
2	7.994(5)	1.0892(11)	0.1(0.7)	1.2(1.1)	0.082	0.044	2.68	1.73
3	7.966(5)	1.0918(29)	−3.5(0.6)	3.7(2.6)	0.077	0.041	1.40	0.90
4	8.061(7)	1.0879(9)	8.4(0.8)	0.1(0.8)	0.077	0.041	3.00	1.94
5	8.060(3)	1.0829(7)	8.3(0.4)	−4.5(0.6)	0.030	0.016	3.59	2.32
6	8.057(3)	1.0841(3)	8.0(0.4)	−3.5(0.3)	0.024	0.013	4.58	2.95
7	7.987(12)	1.0890(9)	−0.8(1.5)	1.1(0.8)	0.081	0.043	1.87	1.21
8	8.060(13)	1.0835(13)	8.4(1.6)	−4.0(1.2)	0.029	0.016	4.02	2.59
9	8.071(8)	1.0852(6)	9.7(1.0)	−2.4(0.5)	0.062	0.033	3.60	2.32
10	8.022(5)	1.0862(10)	3.6(0.6)	−1.5(1.0)	0.119	0.063	2.57	1.66
11	8.074(4)	1.0878(17)	10.1(0.5)	−0.0(1.6)	0.039	0.021	3.07	1.98
12	8.020(14)	1.0867(35)	3.3(1.7)	−1.0(3.2)	0.104	0.056	2.63	1.70
13	8.023(13)	1.0852(22)	3.7(1.6)	−2.4(2.0)	0.116	0.062	1.95	1.26
14	7.992(5)	1.0850(23)	−0.2(0.6)	−2.6(2.1)	0.104	0.056	2.03	1.31
15	8.059(9)	1.0862(8)	8.2(1.1)	−1.5(0.7)	0.042	0.022	2.84	1.83
16	8.102(8)	1.0797(12)	13.5(1.0)	−7.5(1.1)	0.031	0.016	5.30	3.42
17	8.058(10)	1.0880(17)	8.1(1.2)	0.1(1.6)	0.027	0.015	3.29	2.12
18	8.033(8)	1.0894(24)	5.0(1.0)	1.4(2.2)	0.036	0.019	3.09	1.99
19	8.050(5)	1.0879(12)	7.0(0.7)	0.1(1.1)	0.008	0.004	3.15	2.03
20	8.043(10)	1.0862(8)	6.2(1.2)	−1.5(0.8)	0.009	0.005	3.15	2.03
21	8.085(10)	1.0821(8)	11.4(1.3)	−5.3(0.7)	0.041	0.022	4.65	3.00
22	7.995(9)	1.0873(20)	0.2(1.2)	−0.5(1.9)	0.102	0.054	2.36	1.52
23	8.073(5)	1.0811(10)	9.9(0.6)	−6.2(0.9)	0.042	0.022	4.33	2.79
24	8.100(5)	1.0788(7)	13.3(0.6)	−8.3(0.6)	0.009	0.005	6.08	3.92
ALH-77307 (C3)								
1	7.859(4)	1.0780(10)	−16.8(0.5)	−9.1(0.9)	0.017	0.009	3.00	1.94
2	7.858(9)	1.0753(16)	−17.0(1.2)	−11.6(1.5)	0.031	0.017	2.48	1.60
3	7.965(10)	1.0879(12)	−3.6(1.3)	0.1(1.1)	0.016	0.009	3.00	1.94
4	7.974(4)	1.0887(13)	−2.4(0.5)	0.8(1.2)	0.022	0.012	2.84	1.83
5	7.974(7)	1.0875(14)	−2.5(0.9)	−0.3(1.3)	0.016	0.009	2.41	2.20
6	7.948(13)	1.0814(11)	−5.7(1.6)	−5.9(1.0)	0.146	0.078	1.73	1.12
7	8.004(5)	1.0836(2)	1.3(0.7)	−3.9(0.2)	0.054	0.029	3.66	2.36
8	8.019(18)	1.0865(16)	3.2(2.2)	−1.2(1.4)	0.054	0.029	3.70	2.39
9	7.961(5)	1.0815(6)	−4.1(0.6)	−5.9(0.5)	0.079	0.042	2.97	1.92

R24/25: $^{24}Mg/^{25}Mg$, R26/25: $^{26}Mg/^{25}Mg$, R27/24: $^{27}Al^+/^{24}Mg^+$, R24/28: $^{24}Mg^+/^{28}Si^+$.
Δ24/25 and Δ26/25 were calculated by eq. (1).
Atomic ratios of Al/Mg and Mg/Si were calculated by eqs. (2) and (3).
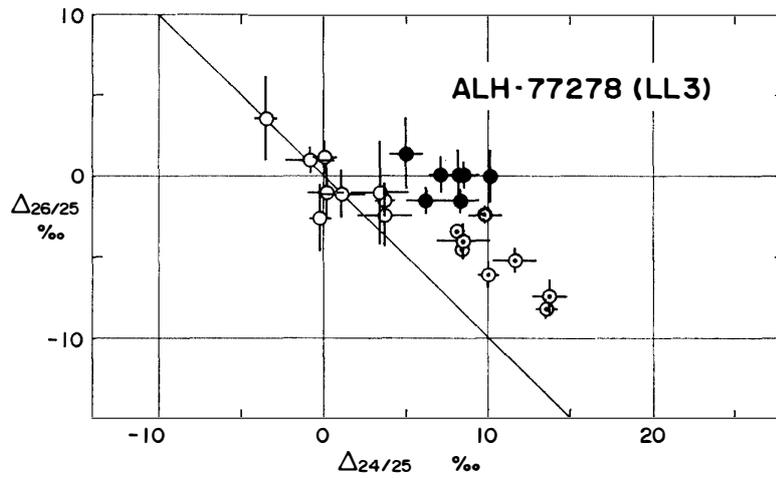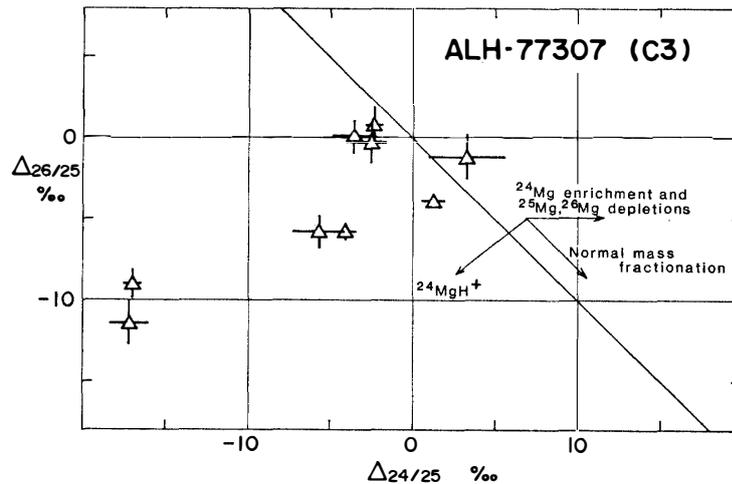Errors in ( ) are standard deviations of the mean.

Fig. 1. Three isotope plot of magnesium for the specimen of ALH-77278 (LL3) chondrite. The origin corresponds to the isotopic ratios for the terrestrial forsterite (laboratory standard) from Ehime Pref., Japan. The straight line with the slope of −1 represents the normal mass fractionation line. ○ : Mg/Si≤1.8, ● : 1.8< Mg/Si <2.2, ⊙ : 2.2≤Mg/Si. Al/Mg <0.1.

Fig. 2. Three isotope plot of magnesium for the specimen of ALH-77307 (C3) chondrite. The origin corresponds to the isotopic ratios for the terrestrial forsterite (laboratory standard) from Ehime Pref., Japan. The straight line with the slope of −1 represents the normal mass fractionation line. Al/Mg <0.1.

and $^{24}Mg^+/^{28}Si^+$. These atomic ratios were calculated from the intensity ratios by the use of calibration curves* for Al/Mg and Mg/Si obtained for several terrestrial samples according to eqs. (2) and (3).

$$Al/Mg = (^{27}Al^+/^{24}Mg^+) \times 0.53, \qquad (2)$$

$$Mg/Si = (^{24}Mg^+/^{28}Si^+) \times 0.65. \qquad (3)$$

* The atomic concentrations of these elements were measured by atomic absorption spectrometry.

Figures 1 and 2 are three isotope plots and a straight line with the slope of -1 in each figure corresponds to the normal mass fractionation line through the point of laboratory standard forsterite. The abscissa represents $\Delta_{24/25}$, and the ordinate $\Delta_{26/25}$ in permil.

3.1. ALH-77278

In Fig. 1, three groups of data are plotted. Those are (I) for the portions where the concentration ratio of Mg/Si is lower than 1.8, (II) for the portions, Mg/Si between 1.8 and 2.2, and (III) for the portions, Mg/Si higher than 2.2.

In the case of group (I), the plotted points are along the normal mass fractionation line within the statistical errors, and there are neither excesses nor depletions of Mg isotopes after the correction for the normal mass fractionation.

In the case of group (II), almost all points deviate from the origin to the positive direction of $\Delta_{24/25}$ axis up to about 10 permil, in spite of the fact that the variation in the direction of $\Delta_{26/25}$ axis is less than 3 permil. From the result, the positive anomaly of $\Delta_{24/25}$ can be considered to be due to the addition of ^{24}Mg or the depletions of both ^{25}Mg and ^{26}Mg in nearly the same fractions. The former case is more plausible than the latter. This will be discussed in Subsection 3.4.

In the case of group (III), the plotted points are along the line which is parallel to the normal mass fractionation line, although this line deviates toward the positive $\Delta_{24/25}$. The deviation can be explained as the addition of ^{24}Mg or as the fractionation after the addition of ^{26}Mg.

3.2. ALH-77307

In Fig. 2, the plotted points scatter over a wide range toward the left down direction. The two data shown in the most left down part of the figure were taken for the portions of matrix where a comparatively large mass peak of $^1H^+$ was observed. At those portions, the $^1H^+/^{24}Mg^+$ ratio was about 4×10^{-2}, although this ratio was usually less than 6×10^{-3}. Accordingly, the deviations of the data are considered to result from the contribution of magnesium hydride ions, $^{24}MgH^+$. There are two more data plotted near $(-5, -5)$ point in Fig. 2. Those are also considered to be mainly due to MgH^+ ions.

From the results, these magnesium hydride ions seem to be originated from hydrogen-containing constituents such as H_2O trapped in the specimen.

The plotted points except four data mentioned above concentrate at the origin along the normal mass fractionation line. So, any anomaly of magnesium isotopes has not yet been observed in this sample.

3.3. Terrestrial samples

As reported elsewhere (Nishimura and Okano, 1982), it was confirmed that the data obtained for four terrestrial forsterite-rich olivine samples in lherzolite and spinel lherzolite fell well on a normal mass fractionation line through the point for a laboratory standard forsterite. Therefore, the anomalies of Mg isotopic ratios mentioned in Subsections 3.1 and 3.2 are thought to be intrinsic.

3.4. Discussion about anomalous $\Delta_{24/25}$

For the ALH-77278 specimen mentioned in Subsection 3.1, the data corresponding to group (II) have positive anomalies of $\Delta_{24/25}$ as shown in Fig. 1. This can be due to the addition of ^{24}Mg or the depletions of ^{25}Mg and ^{26}Mg in nearly the same fractions.

Possibilities of apparent increase by overlapping of molecular ionic species to the peak at mass 24 and possibilities of a few mechanisms decreasing ^{25}Mg and ^{26}Mg are discussed in the following.

3.4.1. Possibility of contribution of $^{23}NaH^+$

The contribution of $^{23}NaH^+$ to the peak at mass 24 was estimated from mass spectra obtained for a terrestrial sodium-rich feldspar in granodiorite from Hyogo Pref., Japan. Since the peak at mass 24 essentially consists of $^{24}Mg^+$ and $^{23}NaH^+$ in this case, $^{23}NaH^+$ was evaluated by subtracting the contribution of $^{24}Mg^+$ from the peak at mass 24. The contribution of $^{24}Mg^+$ can be estimated from the peak appearing at mass 25 ($^{25}Mg^+$). In almost all cases, no residue of the subtraction of $^{24}Mg^+$ from the peak at mass 24 has existed and the maximum value of $^{23}NaH^+/^{23}Na^+$ was found to be 5×10^{-5}.

Although the $^{23}Na^+/^{24}Mg^+$ ratio was of the order of 1000 in the case of the feldspar sample, the ratio was less than 0.05 for the analyzed portions of the chondrites. Therefore, the contribution of $^{23}NaH^+$ to $^{24}Mg^+$ was estimated to be less than 2.5×10^{-6} in the present work.

From the above result, the anomaly of $\Delta_{24/25}$ was hardly thought to be originated from the contribution of $^{23}NaH^+$.

3.4.2. Contributions of $^{48}Ti^{2+}$, $^{48}Ca^{2+}$ and $^{12}C_2^+$

Contributions of these species have been extensively studied, and the order of the contributions was estimated to be less than 1.2×10^{-4} as a whole as described in the previous paper (NISHIMURA and OKANO, 1982).

3.4.3 Possibility of depletions of ^{25}Mg and ^{26}Mg

There is little possibility to decrease both ^{25}Mg and ^{26}Mg in nearly the same fractions as far as nuclear reactions are concerned.

Other than nuclear reactions, apparent depletions of isotopes can be caused by fractionations, which are considered to be due to sputtering, chemical processes such as diffusion, vaporization and dissociation.

As for the sputtering, fractionation have been reported to be mass-dependent and the light isotope is preferentially sputtered (RUSSELL et al., 1980; SLODZIAN et al., 1980; SHIMIZU and HART, 1982; ARAI et al., 1979). Therefore, the possibility of the depletions due to sputtering is excluded.

Moreover, it is usually considered that the fractionations originated from diffusion and vaporization are also mass-dependent and the fractionation factors are inversely proportional to the square root of the mass, and these possibilities are also excluded.

Another possibility for nearly the same order depletions of ^{25}Mg and ^{26}Mg is due to dissociation and decomposition as in the case of oxygen isotopes (HEIDENREICH and THIEMENS, 1983).

They reported that when ozone was produced from oxygen gas in an O_2 reservoir by electric discharge and the ozone was collected on the cold surface, non-mass-de-

pendent fractionation by the same fractions of ^{17}O and ^{18}O against ^{16}O was observed. And this fractionation has the similar tendency to the variation of isotopic composition due to the addition of almost pure ^{16}O to the original oxygen with cosmic abundance.

However, we consider the production of Mg-containing minerals such as spinel and forsterite from atoms of Al, Si and O. From the cosmic abundances of Mg and O, the production probability of MgO molecules is expected to be more than 100 times higher than that of Mg_2. And even if those molecules were dissoicated by ultraviolet photons as in the case of O_2 molecules, a fraction of Mg photo-dissociated from Mg_2 would be negligibly small. Therefore, the effect of the non-mass-dependent fractionation coming from the symmetry of molecules can be excluded.

From these considerations, the positive anomaly of $\Delta_{24/25}$ for group (II) is most plausibly concluded to be due to the addition of practically pure ^{24}Mg.

3.5. Estimate of mineral with excess ^{24}Mg

In order to estimate a mineral, known terrestrial minerals have been analyzed and the ratios of Al/Mg and Mg/Si were evaluated from the secondary ion intensities by
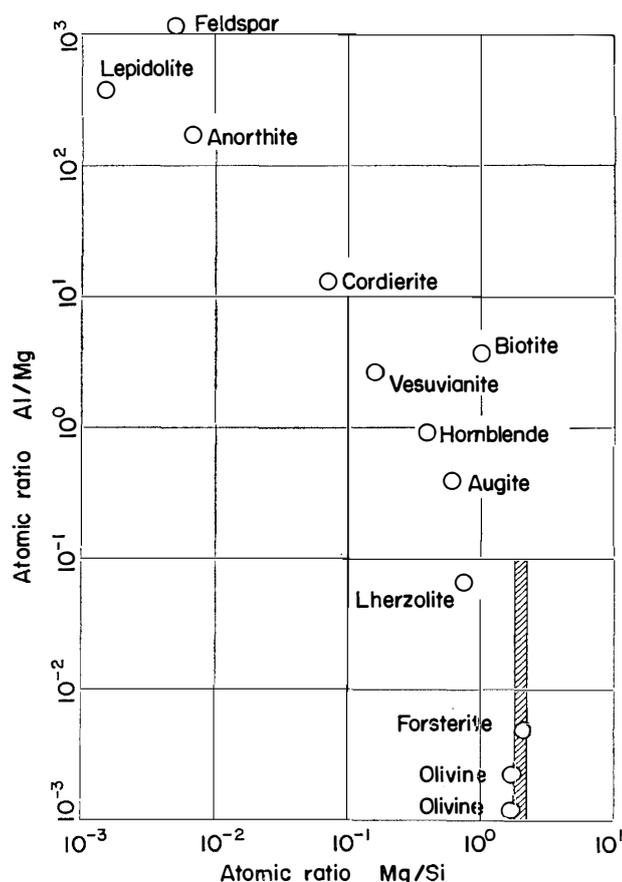

Fig. 3. Atomic ratios Al/Mg versus Mg/Si obtained for several known terrestrial mineral samples. Atomic concentrations were calculated by using calibration curves obtained by atomic absorption spectrometry and by secondary ion mass spectrometry.

using eqs. (2) and (3). In Fig. 3, is shown a plot of Al/Mg versus Mg/Si for various kinds of minerals. In the same figure, an area corresponding to the data of group (II) for ALH-77278 is shown by hatching. From this figure, possible minerals corresponding to the analyzed portions are estimated to be mainly forsterite-rich olivine, although many kinds of minerals are considered to conglomerate in the analyzed area because the radius of the area is about $100\,\mu$m and is in the matrix of the chondrite.

In addition, one of the previously reported portions* of the Yamato-74191 (L3) meteorite (NISHIMURA and OKANO, 1982) has been analyzed for Mg and Si by EPMA. Then the content of Mg was measured to be 27 atomic percent and Si 13, atomic percent, and this portion was concluded to be forsterite. For this portion, Al/Mg is less than 0.07 and Mg/Si is 1.87 from the secondary ion mass spectrum, and the ratio is plotted within the hatched area of Fig. 3.

4. Conclusion

In the case of ALH-77278(LL3), clear excesses of ^{24}Mg have been observed for the portions of matrix area where the concentration ratio of Mg/Si is between 1.8 and 2.2 and that of Al/Mg is less than 0.1. These portions are thought to be forsterite-rich olivine from the comparison among mass spectra for the sample and terrestrial minerals. This excess ^{24}Mg together with the previously reported results of the excess ^{24}Mg in the Allende and Yamato-74191 chondrites (NISHIMURA and OKANO, 1981a, b, 1982) can be evidences that the primordial solar nebula was isotopically inhomogeneous and consisted of at least two components. One of them is an original component with cosmic isotopic abundances and another is additional component which is considered to be formed by a supernova having exploded $1–3 \times 10^6$ years prior to the crystallization of minerals in primitive meteorite and injected into the pre-existed solar nebula.

For the sample of ALH-77307 (C3) chondrite, any isotopic anomaly of magnesium has not yet been found.

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* For this portion, 13 permil ^{24}Mg excess has been detected.

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